

SANDIA REPORT

SAND2000-3001

Unlimited Release

Printed December 2000

New Glass Technologies for Enhanced Architectural Surety[®]: Engineered Stress Profiles (ESP) in Soda-Lime-Silica Glass

S. Jill Glass, Matthew Abrams, and Rudolph V. Matalucci

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States
Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Prices available from (703) 605-6000
Web site: <http://www.ntis.gov/ordering.htm>

Available to the public from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A04
Microfiche copy: A01



New Glass Technologies for Enhanced Architectural Surety[®]: Engineered Stress Profiles (ESP) in Soda-Lime-Silica Glass

S. Jill Glass, Principal Investigator, and Matthew Abrams^a
Ceramic Materials Department

Rudolph V. Matalucci, Project Manager
Civilian Physical Surety Technologies Department

Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0782

^a*Current address: Department of Materials Science and Engineering,
Penn State University, University Park, PA*

Abstract

There is growing awareness of the need to protect building occupants from the effects of malevolent acts, extreme weather, and accidental gas explosions in plants and residential dwellings. A large percentage (85%) of the injuries and fatalities caused by terrorist bombings have been attributed to flying window glass. Numerous fixes have been proposed from the empirical database and field testing by the Department of State, the Defense Threat Reduction Agency, the General Services Administration, the Department of Defense, and other government agencies. Some fixes are being implemented by these agencies. This Sandia National Laboratories project explores enhanced glass performance that can reduce injuries and how the glass affects the overall building response. Sandia National Laboratories has conducted initial blast tests on window glass and there are indications that certain designed flaws and engineered features of the glass, including controlled fracture properties, can be applied that could result in fewer fatalities and injuries to building occupants.

Engineered Stress Profile glass with controlled fracture properties was developed recently by researchers at Penn State (Green et al., 1999) and tested at Sandia National Laboratories. This glass has very high reliability (Weibull modulus = 60), strength of 4 to 5 times that of regular glass, and unusual fracture behavior in that multiple, visible warning cracks are generated before catastrophic failure occurs. The glass also fractures into very small fragments. This property is the primary advantage of the use of stressed glass in an architectural application, as small fragments are less lethal than the large shards produced during failure of regular glass. Another advantage of this glass for applications under sustained loads is that it provides a visible warning that it has reached stresses close to its failure load. The enhanced properties and anomalous behavior were achieved using a double ion exchange process on a specialty glass composition.

The overall objective of this program is to evaluate the feasibility of developing a glass material that can be used effectively in blast environments to reduce injuries to building occupants. Understanding the mechanics and processing of Engineered Stress Profile (ESP) glass is a critical part of this evaluation. Several manufacturing processes are being investigated to determine the viability of producing the type of glass that would be blast-resistant or would fail in a less lethal manner (i.e., greater frangibility, controlled strength, etc). The objective of this year's study was to develop a process for producing Engineered Stress Profile glass using commercially available soda-lime-silica glass. The effort from the first year produced a manufacturing process for commercial soda-lime-silica glass that provides potential performance advantages in applications where Architectural Surety® requirements are critical.

Acknowledgments

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the U.S. Department of Energy under contract number DE-AC04-94AL85000. This work was funded by the Laboratory Directed Research and Development Program at Sandia from March 31, 1999, to September 30, 2000.

The help and support of the following individuals has been vital to the success of this research: Prof. David J. Green of Penn State University and Ed Beauchamp, Clay Newton, Lawrence W. Carlson, and Ron Stone of Sandia National Laboratories. Thanks to Sharon O'Connor for invaluable and timely assistance in assembling and organizing the report.

Contents

Abstract.....	3
Acknowledgments.....	5
Contents.....	7
Figures.....	9
Introduction.....	11
<i>Impact of Work</i>	17
Experimental.....	18
<i>Materials and Equipment</i>	18
<i>Sample Preparation</i>	18
<i>Ion-Exchange Processing</i>	18
<i>Optical Stress Measurement</i>	19
<i>Strength Testing</i>	20
Results.....	21
Conclusions.....	22
<i>Future Work</i>	22
References.....	25
Selected Bibliography.....	27
Appendix	34

Figures

<i>Figure 1.</i> Cross Sections of Glass Plates Showing Residual Stress Profiles Due to Thermal and Chemical Modifications.....	11
<i>Figure 2.</i> Schematic Diagram of Ion-Exchange Process.....	12
<i>Figure 3.</i> Stress Profiles of Ion-Exchanged Glass.....	14
<i>Figure 4.</i> Failure Probability vs. Applied Stress for Various Weibull Moduli (m)	15
<i>Figure 5.</i> Detail of 4-Point Bend Specimen.....	18
<i>Figure 6.</i> Schematic of Optical System Used to Measure Retardation in Stressed Glass Samples.....	19
<i>Figure 7.</i> Change in Central Tension Measured as Surfaces Are Removed by Acid Etching.....	20
<i>Figure 8.</i> Strengths for Processed SLS Glass.....	21
<i>Figure 9.</i> Tensile surface of SLS Glass Bend Bar at a) 60% of Fracture Stress and) 85% of Fracture Stress.....	22
<i>Figure 10.</i> Stress Profile Measurements Using Optical Retardation.....	22
<i>Figure 11.</i> Partial Stress Profile for Sample with Extended 2 nd Ion-Exchange.....	23

Introduction

Use of glass as an engineering material is limited by its brittle fracture behavior, wide strength variation, and low effective strength under normal use conditions. These characteristics were described by Griffith (1920, 1924) as a result of surface cracks and other flaws in the material that act as stress concentrators. Glass strength is normally controlled by the size of the worst defect, which varies considerably from sample to sample. The larger the crack, the lower the stress is required for it to propagate. The implications of the presence of a large population of flaws are that glass fractures catastrophically, usually at stresses more than one hundred times lower than the theoretical strength, and the variability in the stresses that lead to failure is very high ($\pm 25\%$) (Glass, 1993). The combination of low strength and high strength variability means that engineers who design for applications that could use glass either use very thick glass to achieve high safety factors or decide not to use glass at all.

One technique that has been used to overcome the low strength of glass is to induce a compressive stress in its surface. Two processes have been employed to achieve this stress: either a thermal tempering process, by which the surface is cooled more rapidly than the interior, or an ion exchange process, in which larger ions are substituted for smaller ions in the surface. (This chemical process is often called ion stuffing.) The types of stress profiles that are generated by these two processes are shown in Figure 1.

Stress Profiles in Conventionally Strengthened Glass

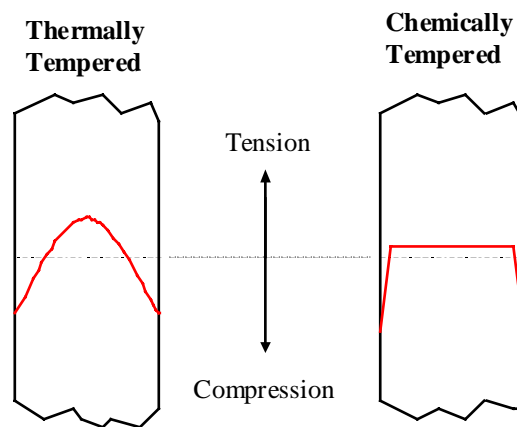


Figure 1. Cross Sections of Glass Plates Showing Residual Stress Profiles Due to Thermal and Chemical Modifications

In the ion-stuffing method of compressive strengthening (Figure 2), small alkali ions in the glass are replaced by larger ions. Thus sodium can replace lithium; potassium or silver can replace sodium, etc. The larger replacement ions take up more volume than the original ions. When the ion-exchanged section is constrained by adjacent non-exchanged glass, it cannot expand to its new natural volume. Instead it develops a compressive stress at the surface, balanced by tensile stress in the non-exchanged region.

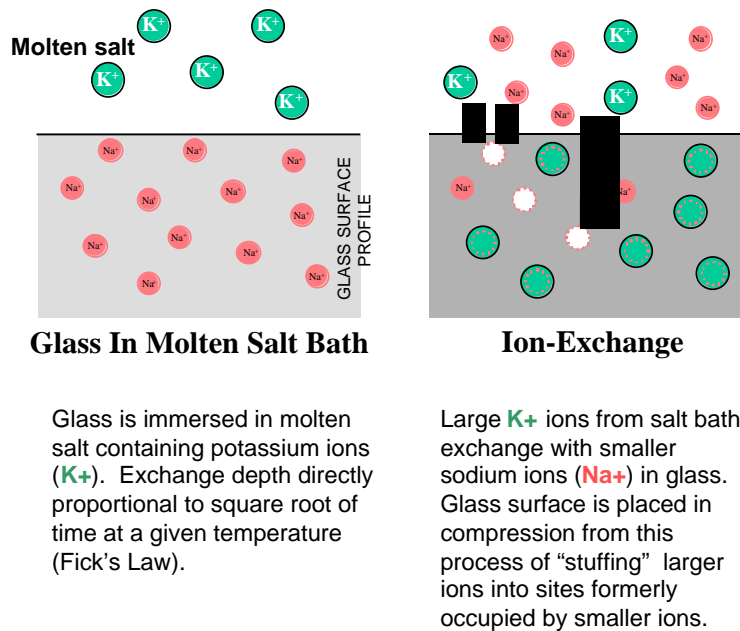


Figure 2. Schematic Diagram of Ion-Exchange Process

Because cracks normally grow under tension, applied tensile stresses must overcome the residual compression in the surface of the glass in order to cause failure. The degree of strengthening can be more than three times the as-received level (Zijlstra and Burggraaf, 1968). One of the other benefits of compressive strengthening, especially for safety critical applications such as automobile windows and architectural glazing, is that when failure occurs, the glass fragments are much smaller and less shard-like (and hence less lethal) than in regular annealed glass.

Many commercial and defense applications of glasses require high strength; however, the fracture pattern, fragment size, and strength variability, as well as how to control each of these characteristics, have largely been ignored. Although fragments are smaller for glasses with compressive surface stresses than for stress-free glasses, they are still too large for Architectural Surety[®] and other applications of interest. In the past, the only method for controlling glass fragment size has been to try to control the level of interior tension; no efforts have been made to control the fragment shape. In some circumstances, because of the difficulty in controlling the process used to produce the surface compression and the nature of the fracture process itself, the glass does not always completely disintegrate into small fragments, resulting in large joined assemblages of glass fragments (Beauchamp and Matalucci, 1998).

The major problem with using a surface compression strengthening technique is that the strength variability often increases for compression-strengthened glass compared to as-received glass; the strength variability of ceramics and glasses is already unacceptably large for many applications!

Currently there is wide interest in the behavior of glass in windows (Blast Effects Mitigation and Injury Outcomes Conference, 2000) and other applications in which control of the fragmentation behavior (smaller and controlled fragment sizes), increased strength, and a significant reduction in the strength variability are desired. Other applications of glass require that it fractures at a very narrowly defined range of stresses and that it fragment into numerous microscopic fragments. These applications include removable valves for the oil industry, architectural glazing to protect building occupants against terrorist bombings, and several defense program uses.

Strategies for increasing the strength and decreasing the strength variability of polycrystalline ceramics are now well known, but there has been little work on doing the same for glasses. One approach for polycrystalline ceramics has been to use microstructural modifications, such as fiber and grain bridging, that produce R-curve behavior (increasing crack resistance) in the material. These modifications produce an apparent increase in the toughness of the material as cracks in it grow. Because glass does not have a microstructure, similar strategies are unavailable. Also, many of the reinforcement strategies used for polycrystalline ceramics are not an option for glasses in which the transparency of the glass is also often an essential feature of its application.

One option in glass has been to design a built-in stress profile that would produce R-curve behavior. Stress profiles have been produced in glass for many years using both ion exchange and thermal tempering processes; however, until recent theoretical analyses were conducted it was not clear what kinds of stress profiles could be used to improve both the strength and the reliability and to produce flaw-insensitive behavior. We now have the theoretical analyses that show what types of profiles will produce the desired behavior. A recent theoretical approach proposed by Tandon and Green (1991 and 1992) suggested that the strength variability of ion exchanged or tempered glass can be very tightly controlled by tailoring the stress profiles to produce the compressive stress maximum below the surface, rather than at the surface. They suggested that certain surface stress profiles would allow a crack to be arrested and that there would be a reduction in the strength variability.

One demonstrated way to achieve the desired stress profile is to use a two-step ion exchange process (Sglavo et al., preliminary patent disclosure to produce an Engineered Stress Profile (ESP) in which there is a high compressive stress just below the glass surface, rather than at the surface. (see Figure 3). According to work by Green (1984), the extent of the compressive layer below the glass surface has a significant effect on the strength and reliability, often more important than the level of maximum compressive stress.

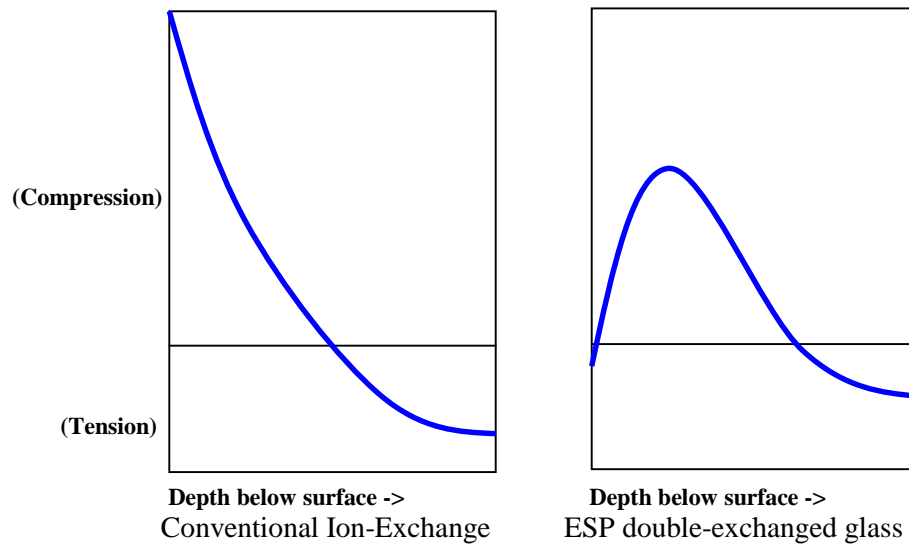


Figure 3. Stress Profiles of Ion-Exchanged Glass

In experiments by Green et al. (1999 and 1999) and Sglavo and Green (in prep.), this type of 'buried' compressive stress profile has shown a number of beneficial effects in terms of strength, reliability, flaw-tolerance, and fracture behavior. The double ion exchange process was demonstrated on a specialty glass (sodium aluminosilicate). In the first step, potassium ions from a molten salt bath were exchanged for sodium ions in the glass. In the second step, some of the introduced potassium was removed from the surface by an exchange with sodium ions. Strengths were measured for glasses made in this manner and very low strength variability was observed (Green et al., 1999; Green et al., 1999; Glass et al., 2000). The glass has strength four to five times that of regular glass and Weibull modulus values as high as 60. The benefits of a Weibull modulus at this level are shown in Figure 4. A designer's confidence in the glass's ability to survive or fail at a given stress is increased significantly with higher Weibull modulus. For an application in which the glass must sustain 80% of the average failure stress, ESP glass with a Weibull modulus of 60 has only a one or two in one million chance of failing. In contrast, regular annealed glass (Weibull modulus = 5) has a 30% failure probability.

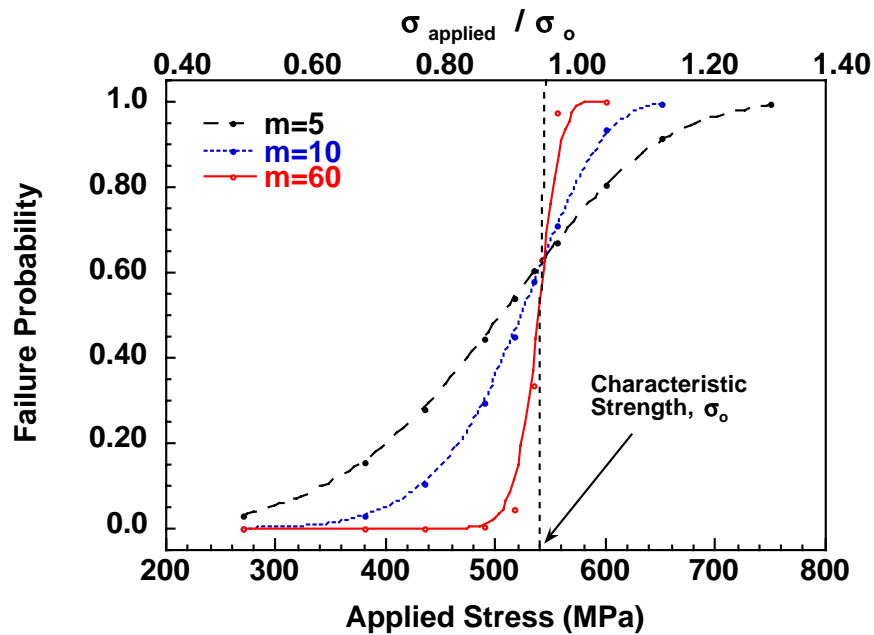


Figure 4. Failure Probability vs. Applied Stress for Various Weibull Moduli (m) (*ESP glass, with $m = 60$, has a dramatic increase in failure probability only at the average failure stress, in contrast to regular glass, with $m = 5$ to 10 , which has a high failure probability at stresses above and below the characteristic failure stress.*)

The ESP glass also fractures into very small fragments. This is one of the primary advantages of the use of pre-stressed glass in an architectural application, as small fragments are less lethal than the large shards produced during failure of regular glass. Also, during strength testing, cracks could be seen growing in the surface of the glass and then arresting. An increased load was required to initiate the next crack. It propagated slowly and then arrested. This process continued until there was a visible array of cracks indicating that failure was imminent. The material shows some 'fail-safe' behavior, even though it is a brittle material. Such behavior is extremely unusual and could be exploited in many technological applications of glass.

Added benefits of the high strength and reliability are that there would be less breakage during installation and that thinner glass could be used, resulting in reduced cost and weight. If overall Architectural Surety® considerations dictate that the windows not be strengthened to this degree, the strength can be reliably controlled to achieve a consistent value that is lower, but still stronger than regular glazing if that proves to be beneficial. Another advantage of a high-strength glass with low strength variability is that an actuator could be incorporated into the design of the frame that would cause the glass to fail at a very specific pressure under explosive loading. This would relieve some of the load on the overall structure and cause glass failure before it gains a significant amount of the strain energy that carries fragments into the building.

The goal of the present study was to develop Engineered Stress Profiles (ESPs) in soda-lime-silica (SLS) glass to achieve high strength, low strength variability, and controlled fragmentation. Previous ESP glass research focused on soda-aluminosilicate glasses, which have a higher diffusion rate for alkali ions and therefore offer more rapid, deeper exchange. However, aluminosilicate glasses are produced in relatively small quantities at considerable expense and are used only for specialty applications. Although the double ion exchange method has been successfully used for a specialty glass composition, modified techniques may be required for SLS glasses because of the low diffusion coefficients of the ions in this glass during the ion exchange process. Techniques such as ion implantation or field-assisted exchange could be used to introduce ions that are not readily exchanged using a molten salt bath, or to produce modified surfaces with very controlled depths.

The effects of the ESPs on the strength, strength variability, and fragmentation behavior will be studied for SLS glass for different types of loading conditions, both in terms of the type of loading (e.g., flexural vs. tensile) and the loading duration (sustained, static, dynamic, and explosive loading). The effect of loading rate is very important at both ends of the scale and is not understood under very rapid loading rates, especially for glasses with compressive surface stresses. As the surfaces of glasses usually contain numerous flaws with different sizes and character, their effects on the behavior of the glass and their interactions with each other and the residual stress field during stable crack propagation also need to be evaluated.

The ultimate goal of this program is to understand the behavior and benefits of using ESP glass in Architectural Surety® applications to improve our ability to protect personnel against terrorist activities, such as bombings of federal buildings and extreme weather conditions. We also expect to demonstrate that a new class of glasses can be produced with highly controlled fracture properties that will provide unique capabilities for Defense Programs and commercial applications. The increased reliability of the glass also increases the confidence of designers in the use of glass for both conventional and innovative applications. By developing an ESP process for widely available SLS window glass, ESP glass products can be applied to larger markets at reduced cost, thus changing a limited-use, specialty product into one that can benefit many industries and individuals. Our efforts include developing collaborations with glass manufacturers and the architects, design engineers, and agencies interested in the use of glass, especially in applications in which personnel safety can be enhanced through using a glass with improved properties.

Impact of Work

Validated information about glass behavior and options for enhancing glass performance are important for glass manufacturers; users in the transportation, food and oil industries; Architectural Surety® applications; and defense program applications. For example, automotive glass producers are very interested in how to fabricate glasses that fracture into small fragments with a narrow fragment size distribution. The food packaging industry is interested in reducing the weight of glass containers without jeopardizing consumer safety. Halliburton Energy Services has supported work at Sandia National Laboratories on removable valves. There is considerable interest in Architectural Surety® for ensuring that windows do not fail, or fail in a graceful manner, under extreme weather conditions or terrorist attack. There are similar interests in either ensuring or preventing failure of brittle materials for defense program applications, such as stronglinks and weaklinks.

To be able to design with a glass material that can be counted on to fail or survive in specified conditions will provide unique opportunities in weapons systems and numerous commercial applications. This work will also extend our capabilities for understanding brittle fracture under complex loading conditions.

Experimental

Materials and Equipment

The glass used in the experiments is Starphire, an architectural window glass manufactured by PPG Industries, Inc. with the composition 73% SiO₂, 15% Na₂O, 10% CaO, and 2% trace elements by weight.

Mini-30 and Mini-60 Salt Bath Furnaces from Kirk Optical Co. were used for ion-exchange, as well as conventional laboratory furnaces with welded nickel salt bath vessels. Within the vessels, samples were held in stainless steel wire-mesh racks. Temperature was measured by electrically isolated K-type thermocouples attached to the sample racks.

Sample Preparation

The samples (see Figure 5) used in these experiments were cut from annealed 3.2-mm-thick Starphire SLS glass sheet using a diamond saw, prior to ion-exchange treatment. Biaxial flexure specimens were cut as 25-mm squares. Four-point bend specimens were cut to dimensions of 75 mm by 6.5 mm. The tensile edges of the 4-point bend specimens were then ground to a rounded profile by wet grinding on an abrasive belt.

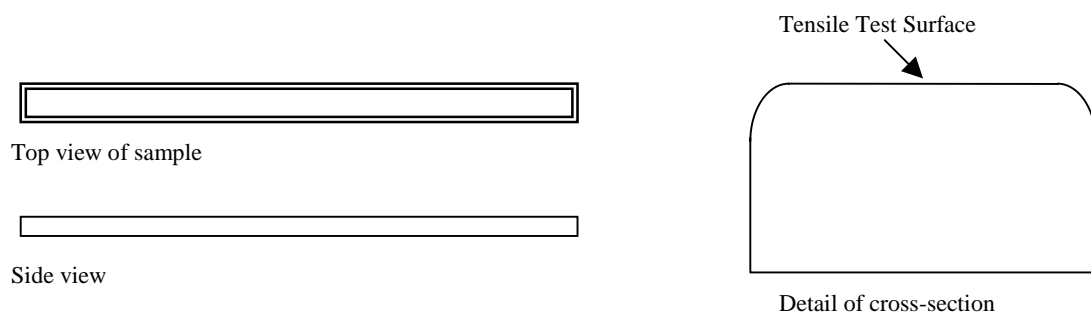


Figure 5. Detail of 4-Point Bend Specimen

Previous work has shown that sample preparation is very important in achieving good results with ESP glass. In particular, corners of the tensile surface must be rounded in order to prevent premature failure from corner cracks during bend testing.

Ion-Exchange Processing

The samples were placed in a stainless-steel wire-mesh carrier, dried in air, and put in a bath of molten potassium nitrate (KNO₃, 99.9% purity) at 450 °C for 48 hours. Temperature was measured using a thermocouple inserted into the wire carrier. Previous work (Abrams and Green, unpublished) showed that these conditions had the potential for producing desirable stress profiles. The samples were held in heated air within the furnace for 15 minutes before and after treatment in order to prevent fracture from thermal shock.

After cooling, the samples were washed in water to remove any residual salt, dried, then placed in the second ion-exchange bath, with a composition of 2 parts KNO_3 to 1 part NaNO_3 by mass, at a temperature of 400 °C for 30 minutes. It is this second ion-exchange process that reduces the potassium concentration at the glass surface, producing the characteristic hump in the ESP glass stress profile.

Optical Stress Measurement

In order to accurately measure the stress distribution in the processed samples, an optical retardation technique was used. Because stressed glass is birefringent, showing a change in refractive index proportional to stress, the stress can be determined by measuring the birefringence for a sample of given length, using techniques by Beauchamp and Altherr (1971).

The experimental setup (see Figure 6) utilizes a sample placed between crossed polarizing filters. The birefringence caused by the stresses within the sample retards and changes the polarization of light passing through it, allowing light to be seen at the far end. The degree of retardation can be accurately measured using a Babinet compensator and a set of optical retarder plates.

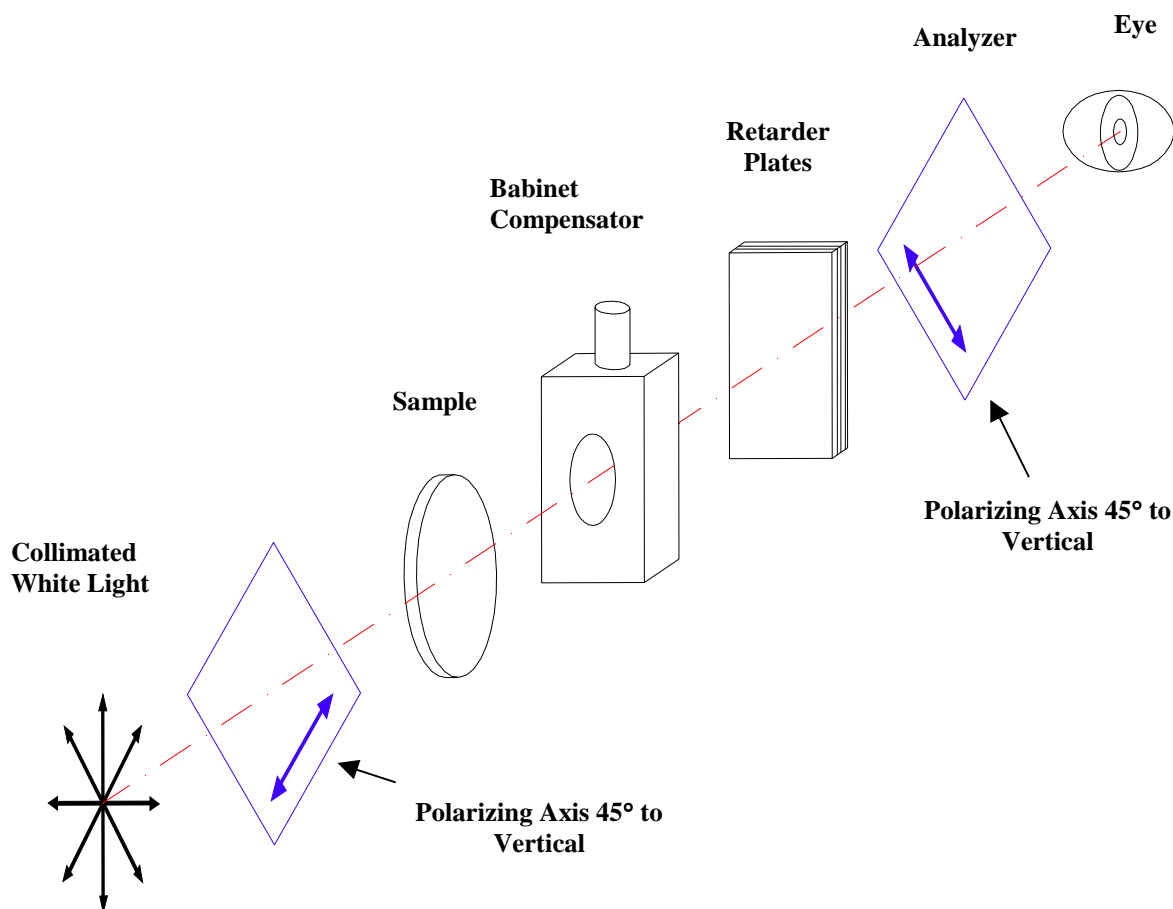


Figure 6. Schematic of Optical System Used to Measure Retardation in Stressed Glass Samples

Because the compressive layer near the surface of the glass is relatively narrow, on the order of ~50 microns, it is difficult to optically observe the birefringence it produces directly. Instead, the birefringence due to the balancing tension at the center of the glass is measured, and the change in central tension is observed as outer layers are etched away in HF acid, as shown in Figure 7.

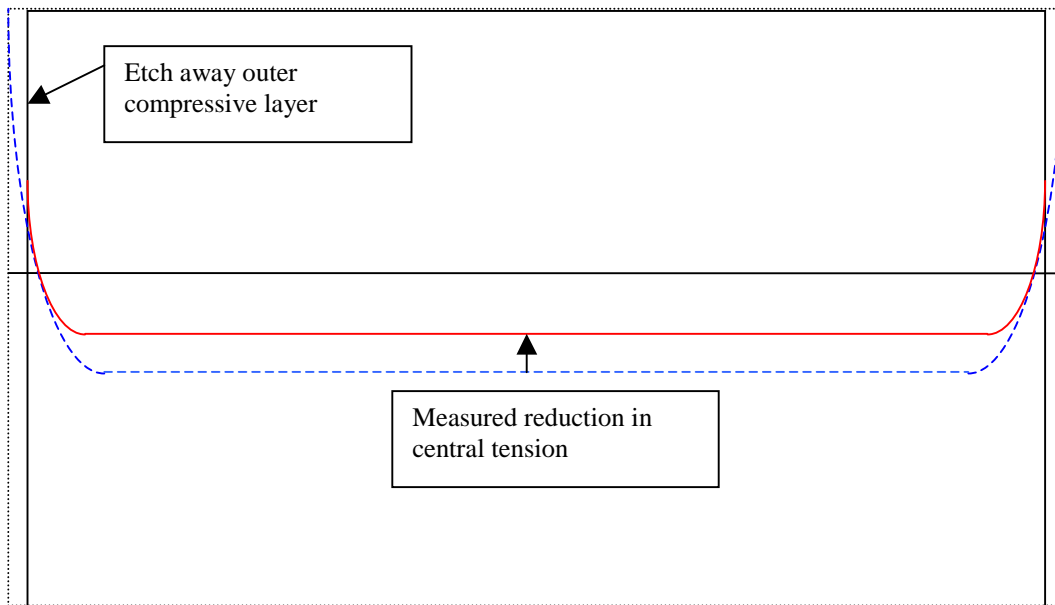


Figure 7. Change in Central Tension Measured as Surfaces Are Removed by Acid Etching

Strength Testing

Mechanical strength testing, including conventional 4-point bend testing and ring-on-ring biaxial flexure testing, was used to measure the strength of ESP glass specimens. Several 4-point bend specimens were not tested to failure, but were instead loaded to specific stress levels, then unloaded and etched with HF acid to reveal any crack patterns that developed prior to final fracture.

Results

The following graph (Figure 8) compares strengthsh for soda-lime-silica glass in the annealed state, after a conventional ion-exchange, and after a double ion exchange (ESP glass), using the ion exchange conditions specified earlier.

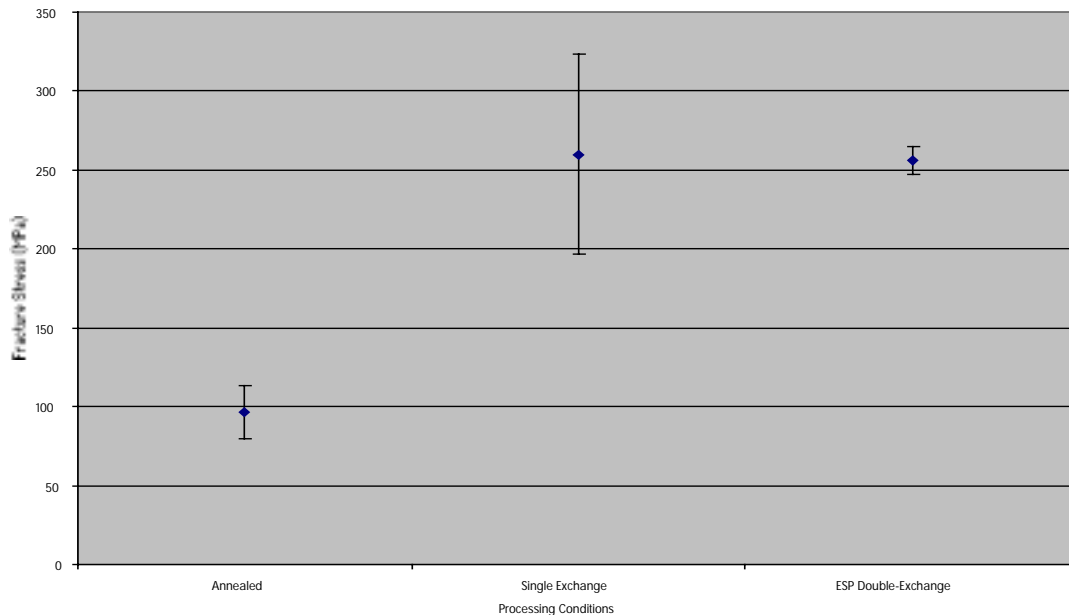


Figure 8. Strengths for Processed SLS Glass

Note that the ESP glass shows high strength as well as very good reliability, with a standard of deviation at ~3% of mean value, a very low value relative to the annealed and single exchange conditions.

The presence of multiple small cracks, which develop in the glass as it approaches fracture stress indicate that the strength of the glass is insensitive to the size of the largest flaws. Below are photographs (Figure 9) of ESP glass, stressed in 4-point bending, then etched to help reveal patterns of multiple, parallel cracks. This cracking effect begins at less than 50% of the mean fracture stress and continues as the applied stress increases, reaching an average spacing of 92 microns at 90% of the fracture stress. Note that without etching the cracks become visible to the naked eye at 85-95% of fracture stress, providing a useful warning of imminent failure.

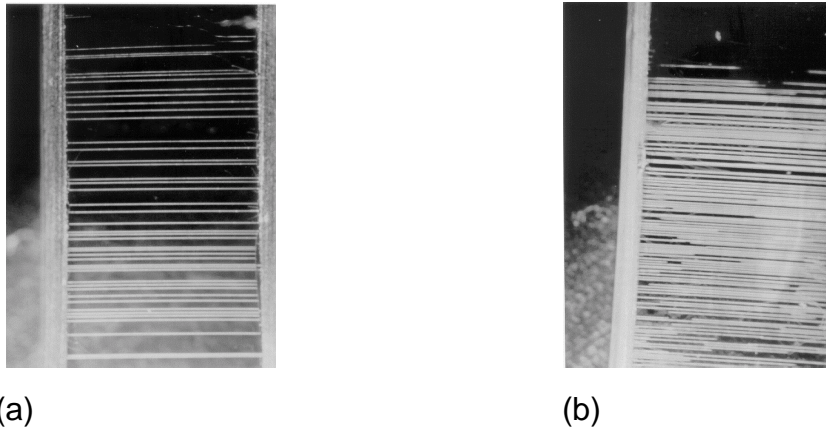


Figure 9. Tensile Surface of SLG Glass at a) 60% of Fracture Stress and b) 85% of Fracture Stress

Figure 10 shows the stress profile for an ESP glass sample, obtained using optical retardation measurements. Note the increasing compressive stress below the surface, with a maximum at approximately 11 microns in depth.

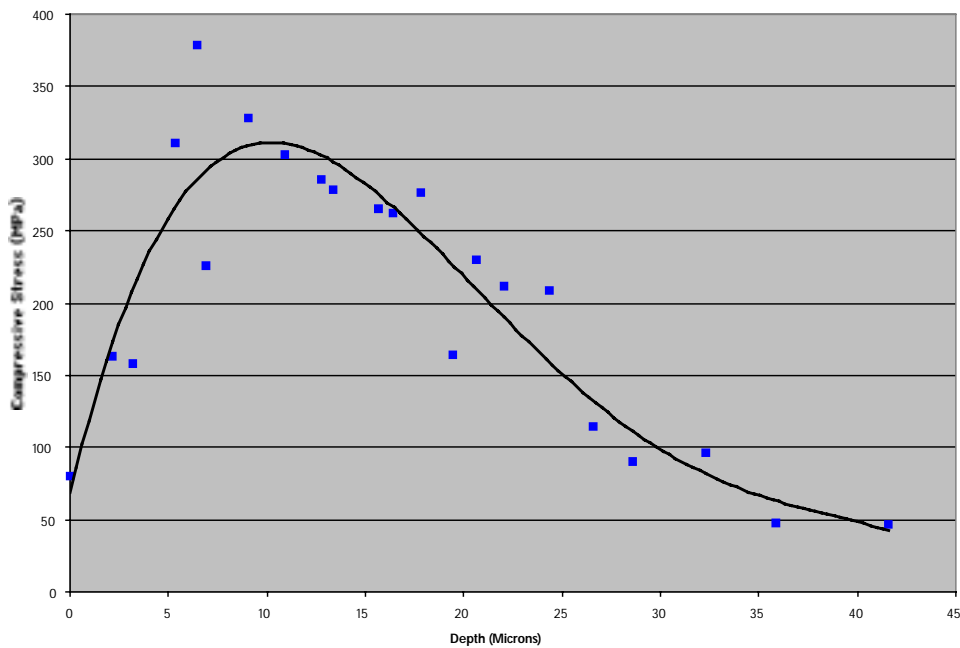


Figure 10. Stress Profile Measurements Using Optical Retardation (Central tension ~5 MPa)

Figure 11 shows a partial stress profile for ESP glass with an extended 2nd exchange treatment, 45 minutes instead of 30. The position of the compressive peak has shifted deeper (~18 μm) beneath the glass surface, as expected. Control of the duration, temperature, and bath composition of each exchange step provides a great degree of control over the peak size, shape, and depth below the surface, allowing a wide range of useful properties.

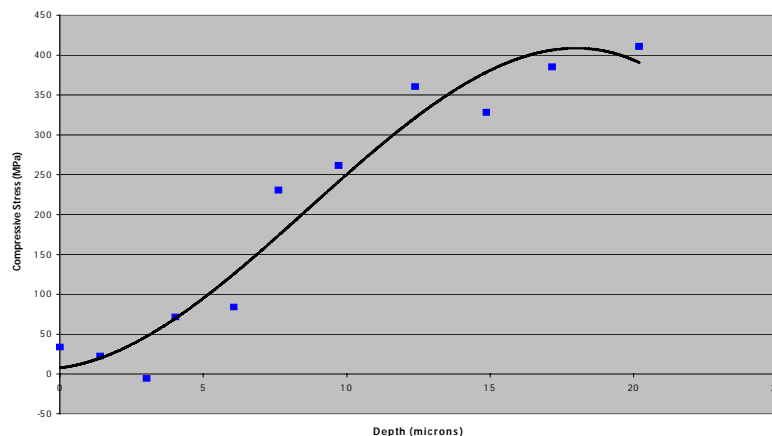


Figure 11. Partial Stress Profile for Sample with Extended 2nd Ion-Exchange (Central tension ~5 MPa)

Previous fracture strength measurements of soda-aluminosilicate ESP glass made at various loading rates showed an unusual increase in strength for slower loading. Preliminary results with SLS ESP glass appear to indicate the same strength increase. This effect is opposite to the loading-rate effects observed in conventional, annealed, tempered, or chemically strengthened glass (Hagy, 1966) and represents another opportunity for future study.

Preliminary work on the abrasion resistance of ESP glass using ball mill abrasion tests as per ASTM C 158 indicated that ESP glass does not significantly lose strength after abrasion by silicon carbide particles. Although scratches are observed on the glass surface, 4-point-bend strength appears unaffected. The interaction of abrasion damage with the multiple cracks normally developed in the glass under high stress is unknown and requires further study.

Conclusions

SLS ESP glass shows high strength with exceptional reliability in 4-point bend testing, with standard deviation at 2-3% of the mean fracture stress. This quality makes it useful for structural and new applications, significantly reducing the chance of failure at low stresses and ensuring failure above a critical stress level. This high reliability can be useful for “command-break” applications such as valves, where it is necessary that the material fracture at a particular stress level.

The multiple cracking patterns shown by ESP glass before fracture provide a progressive warning prior to failure, something very uncommon in glass and ceramic components. Further study is needed to determine what parameters control the number and depth of the cracks and how they affect the unusual mechanical properties of the material.

Results show that by changing ion-exchange processing parameters, the stress profile present in the final glass can be carefully controlled. Theoretically, by driving the profile more deeply below the surface, excellent abrasion resistance can be obtained. By raising the maximum stress, higher strength is achieved. Further work is required to more closely understand the relationship between ion-exchange time, bath composition and temperature; and the final properties of the strengthened glass.

The two-step ion exchange process provides broad flexibility in terms of engineering the stress profile to optimize strength, reliability, and fragmentation behavior for different glass compositions. We will continue to improve our ability to engineer stress profiles and glass behavior to satisfy new application requirements and to determine what properties best satisfy requirements for controlled failure under blast loading conditions for Architectural Surety® applications.

Future Work

Future work includes:

- Further stress profiling in ESP glass, to link processing conditions to final stress state
- Fractography of ESP glasses, leading to a better understanding of fracture behavior in these glasses
- Measuring subcritical crack growth and comparing with behavior of aluminosilicate glass
- Testing ESP glass under rapid/explosive loading

References

Abrams, M. and D. J. Green. Unpublished results.

Beauchamp, E. K., and R. H. Altherr. "Stress Determination in Opaque Materials," J. Am. Ceram. Soc., 54 [2] pp. 103-105, 1971.

Beauchamp, E. K., and R. V. Matalucci. "Dynamics of Window Glass Fracture in Explosions," Sandia Report 98-0598, May 1998.

Blast Effects Mitigation and Injury Outcomes Conference, Oklahoma City, OK, April 20-21, 2000.

Glass, S. J. "Ceramics (Mechanical Properties)," pp. 634-658 in Kirk-Othmer Encyclopedia of Chemical Tech., 4th Edition, John Wiley and Sons, Inc., 1993.

Green, D. J. "Compressive Surface Strengthening of Brittle Materials," J. Mater. Sci. 19, pp. 2165-2171, 1984.

Glass, S. J., E. K. Beauchamp, R. Kipp, C. Newton, S. Nicolaysen, R. Reese, R. Stone, and W. Sullivan. "Controlled Fracture of Prestressed Glass or Glass-Ceramic Rupture Disk," Sandia Report 2000-0828.

Green, D. J., R. Tandon, and V. M. Sglavo. "Crack Arrest and Multiple Cracking in Glass Through the Use of Designed Residual Stress Profiles," Science, Vol. 283 (5406), pp. 1292-1295, Feb. 26, 1999.

Green, D. J., V. M. Sglavo, E. K. Beauchamp, and S. J. Glass. "Using Designed Residual Stress Profiles to Produce Flaw-Tolerant Glass," Fracture Mechanics of Ceramics Conf., High Tech Ceramics Research Centre in the Russian Academy of Sciences, Moscow, July 20-22, 1999.

Griffith, A. A. Phil. Trans. R. Soc., A221, 163, 1920.

Griffith, A. A. 1st Int. Cong. Appl. Mechanics, p.55, 1924.

Hagy, H. E. "Design Strength of a Chemically Strengthened Glass," Central Glass and Ceramic Research Institute Bulletin, Vol. 13, No. 1, pp. 29-31, 1966.

Private communication with D. J. Green and M. Abrams.

Sglavo, V. M., and D. J. Green. "Flaw Insensitive Ion-Exchanged Glass: I Theoretical Aspects," I.E.G. paper, draft.

Sglavo, V. M., and D. J. Green. "Flaw Insensitive Ion-Exchanged Glass: II Production and Mechanical Performance," I.E.G. paper, draft.

Sglavo, V. M., R. Tandon, and D. J. Green. Preliminary patent disclosure.

Tandon, R., and D. J. Green. "Crack Stabilization Under the Influence of Residual Compressive Stress," J. Am. Ceram. Soc. 74 [5], pp.1981-1986, 1991.

Tandon, R., and D. J. Green. "The Effect of Crack Growth Stability Induced by Residual Compressive Stresses on Strength Variability," J. Mater. Res., 7[3], pp. 765-771, 1992.

Zijlstra, A. L., and A. J. Burggraaf. "Fracture Phenomena and Strength Properties of Chemically and Physically Strengthened Glass," J. Non-Cryst. Solids, Vol. 1, pp. 49-68, 1968.

Selected Bibliography

The following table presents a list of background material selected from a literature search.

Reviews		
Review - Methods for Improving the Mechanical Properties of Oxide Glasses	W. Donald	J. Mater. Sci., Vol. 24, pp. 4177-208, 1989
Thermal and Chemical Strengthening of Glass- Review and Outlook	H. A. Schaeffer	pp. 469-83 in Strength of Inorganic Glass, C. R. Kurkjian (ed.), Plenum Press (1985)
Windshields		
Safety Performance of a Chemically Strengthened Windshield	L. Patrick, K. Trosien, F. Dupont	Society of Automotive Engineers, Inc.
Pick-Up Truck Rear Window Tempered Glass as a Head Restraint	G. Nyquist, F. Dupont, L. Patrick	Proc Stapp Car Crash Conf, 28th
PPG Develops High-Strength Aircraft Windshield	none listed	The Glass Industry, 1982.
Impact Fracture of Chemically Tempered Glass Helicopter Windshields	F. Camaratta, R. Digenova	J. Am. Ceram. Soc., Vol. 69, 1986.
Window Strength and Failure		
Truly sophisticated glass specifications skillfully tailor products and treatments to meet specific needs.	C. Beall	Construction Specifier, V. 43, #4
A Failure Theory for Window Glass Plates	H. Norville, J. Minor	Advances in Engineering Mechanics
Contribution to the size effect on the strength of flat glass	K. Blank, H. Gruters, K. Hackl	
Window glass research at Texas Tech University	W. Beason, J. Minor	
Glass Strength Evaluation Using Ring-on-Ring tests	H. Norville, J. Minor, F. ASCE	
Strength of new heat treated window glass lites and laminated glass units	H. Norville, P. Bove	Journal of Structural Engineering, Vol. 119, 1993
Failure Strength of Laminated Glass	J. Minor, P. Reznik	Journal of Structural Engineering Vol. 116, 1990
Strength of Weathered Window Glass	H. Norville, J. Minor	Ceramic Bulletin, Vol. 64, 1985
The Strength of New Thermally Tempered Window Glass Lites	H. S. Norville, P. Bove, D. Sheridan	(Book) Glass Research and Testing Lab- TX Tech , 1991

General Surface Compression Stress		
Fracture Phenomena and Strength Properties of Chemically and Physically Strengthened Glass	L. Zijlstra, A. J. Burggraaf	<i>J. Non-Cryst. Solids</i> , Vol. 1, pp. 49-68, 1968.
Strength of Brittle Ceramic Materials	M. Ernsberger	<i>Ceram. Bull.</i> , Vol. 52, No. 3, pp. 240-6, 1973.
Fracture Mechanical Analysis of Self-Fatigue in Surface Compression Strengthened Glass Plates	M. Bakioglu, F. Erdogan, D. P. H. Hasselman,	<i>J. Mater. Sci.</i> , Vol. 11, pp. 1826-34, 1976.
Contact Fracture Resistance of Physically and Chemically Tempered Glass Plates: A Theoretical Model	B. R. Lawn, D. B. Marshall	<i>Phys. and Chem. of Glasses</i> , Vol. 18, No. 1, pp. 7-18, Feb. 1977.
Facteurs Influençant la Fragmentation du Verre Trempé Thermiquement	E. Le Bras, P. Y. Le Daeron	Collected Papers, XIV Intl. Congr. of Glass, pp. 262-9, 1986.
Surface-Compression Strengthened Glasses: Some Properties	H. Perry	Naval Ordnance Laboratory
Residual Stress Determination		
Residual stress determination using strain gage measurements	R. Tandon, D. Green	<i>J. Am. Ceram. Soc.</i> Vol.73, 1990
Use of crack branching data for measuring near-surface residual stresses in tempered glass	J. Conway Jr., J. J. Mecholsky Jr.	<i>J. Am. Ceram. Soc.</i> Vol. 72, No. 9, 1584-87, 1989.
Stress Determination in Opaque Materials	E. K. Beauchamp and R. H. Altherr	<i>J. Am. Ceram. Soc.</i> , 54 [2] pp. 103-105 (1971).
Optical Methods for Stress Measurement in Glass Plates	A. Colombotto, S. Ravarino, and L. Muzii.	<i>Societa Italiana Vetro</i> , pp. 591-6.
Residual Stress Determination Using Strain Gage Measurements	R. Tandon and D. J. Green	<i>J. Am. Ceram. Soc.</i> , Vol. 73, No. 9, pp. 2628-33, 1990.
Ion Exchange		
"Fracture Behavior of Chemically Strengthened Glass in Connection with the Stress Profile	L. Zijlstra and A. J. Burggraaf,	<i>J. Non-Cryst. Solids</i> I, pp. 163-85, 1969.
Ion-Exchange Equilibria between Glass and Molten Salts	M. Garfinkel	<i>J. Phys. Chem</i> , Vol. 72, No. 12, pp. 4175-81, Nov. 1968.
Design Strength of a Chemically Strengthened Glass	H. E. Hagy	Central Glass and Ceramic Research Institute Bulletin," Vol. 13, No. 1, 1966, pp. 29-31.
The Mechanical Strength of Alkali-Aluminosilicate Glasses after Ion Exchange,"	A. J. Burggraaf	PhD Thesis, Technical University Eindhoven, Sept. 1965.

Ion Exchange (continued)		
Stress Profile Characteristics and Mechanical Behaviour of Chemically Strengthened Lithium Magnesium Aluminosilicate Glasses	M. J. C. Hill, I. W. Donald	Glass Tech. Vol. 30, No. 4, pp. 123-7, 1989.
Preparation and Mechanical Behaviour of Some Chemically Strengthened Lithium Magnesium Alumino-Silicate Glasses,	W. Donald and M. J. C. Hill	<i>J. Mater. Sci.</i> , Vol. 23, pp. 2797-809, 1988.
Calculation methods in the study of Ion-exchange strengthening of flat glass	A. Boguslavskee, O. Pukhlik	
Strengthening of Glass	M. Ernsberger	Glass Indus., pp. 483-87, Sept. 1966.
Part Two: Conclusion, Strengthening of Glass	F. M. Ernsberger	The Glass Indus., pp. 542-5, Oct 1966.
Stresses in Glass Produced by Nonuniform Exchange of Monovalent Ions	S. Kistler	<i>J. Am. Ceram. Soc.</i> , Vol. 45, No. 2, pp. 59-68, Feb. 1962.
Chemical Strengthening of Glass-Ceramics in the System $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$	B. Karstetter, R. Voss	J. Am. Ceram. Soc. Vol. 50, #3
Chemical Strengthening of Glass	J. Olcott	
Some aspects of the fracture of chemically strengthened glass	E. Rabinovich	Glass Technology, Vol. 21, #4, 1980
Selection of the Optimal Strengthening Regime for a Glass using an Ion Exchange Method	A. M. Butaiv	
The Mechanical Strength of Glass Substrates * show high Weibull modulus of 50	T. Kasuga, T. Uno, S. Eda, K. Tachiwana, A. J. Ikushima	Glass Tech. Vol. 33, No. 2, pp. 57-59, 1992.
Thinner Triples from Chemically Strengthened Glass	L. Bogatyrev, N. Tikhomirova	Plenum Publishing Corp.
High p Glass Made by Ion Exchange	K. Nakagawa, K. Italya	US Patent
Double Ion Exchange		
Crack Arrest and Multiple Cracking in Glass Through the Use of Designed Residual Stress Profiles	D. J. Green, R. Tandon, and V. M. Sglavo.	Sci., Vol. 283 (5406) pp. 1292-1295, Feb. 26, 1999. http://www.sciencemag.org/cgi/content/full/283/5406/1295
Flaw Insensitive Ion-Exchanged Glass: I Theoretical Aspects	V. M. Sglavo and D. J. Green	I.E.G. paper, draft.
Flaw Insensitive Ion-Exchanged Glass: II Production and Mechanical Performance	V. M. Sglavo and D. J. Green	I.E.G. paper, draft.

Double Ion Exchange <i>(continued)</i>		
Controlled Fracture of Prestressed Glass or Glass-Ceramic Rupture Disk	S. J. Glass, E. K. Beauchamp, R. J. Kipp, C. S. Newton, S. D. Nicolaysen, R. T. Reese, R. G. Stone, and W. N. Sullivan.	Sandia National Labs Report SAND2000-0828, April 2000.
Strengthening and Crack Arrest in Brittle Materials Using Residual Stress	D. J. Green, V. Sglavo, and R. Tandon.	US Patent Application No 09/502,284, PSU Invention Disclosure No. 97-1731.
Using Designed Residual Stress Profiles to Produce Flaw-Tolerant Glass	D. J. Green, V. M. Sglavo, E. K. Beauchamp, and S. J. Glass.	Fracture Mechanics of Ceramics Conf., High Tech Ceramics Research Centre in the Russian Academy of Sciences, Moscow, July 20-22, 1999.
Field-Assisted Ion Exchange		
Residual Stress in Singly and Doubly Ion-Exchanged Glass	E. E. Shaisha and A. R. Cooper	J. Am. Ceram. Soc., 64 [1] 34-36 (1981).
Ion Exchange of Soda-Lime Glass with Univalent Cations	E. E. Shaisha and A. R. Cooper,	J. Am. Ceram. Soc., 64 [5] 278-283 (1981).
The Effect of Field Reversals on Refractive Index Profiles and Stress in Electric Field Assisted K ⁺ -Na ⁺ Ion Exchanged Soda-Lime Glass	S. Batchelor, R. Oven, and D. G. Ashworth	J. Phys. D; Appl. Phys. 31 pp. 390-401 (1998).
Analysis of Field-Assisted Binary Ion Exchange	M. Abou-El-Leil and A. R. Cooper	J. Am. Ceram. Soc., 62 [7-8] (1979).
Fracture Codes		
Prediction of Material strength and fracture of brittle materials using the sphinx smooth particle hydrodynamics code	D. Mandell, C. Winhate , R. Stellingwerf	Engineering Mechanics
Fractography		
Fracture Mirror-Failure Stress relation in weathered and unweathered window glass panels	D. Reed, R. Bradt	Commun. of Am. Ceram. Soc. Nov. 1984
Injuries Due to Flying Glass		
Nuclear Weapons	S. Glasstone, P. Dolan	US Dept. of Defense, and Energy Research and Development Ad.

Miscellaneous		
Detection of Strength-Impairing Surface Flaws in Glass	M. Ernsberger	Proc. Roy. Soc. A, Vol. 257, pp. 213-23, 1960(?).
Methods for improving the mechanical properties of oxide glasses	I.W. Donald	Journal Mater. Sci. , Vol. 24, 1989.
How heat strengthening differs from Tempering	V. Miihkinen,.	Glass Digest, Dec. 1992.
The catastrophic failure of thermally tempered glass caused by small-particle impact	M. Munawar Chaudhri, C. Liangyi	Nature, Vol. 320, 1986.
Dynamic fracture in zone-tempered glasses observed by high-speed photoelastic colour photography.	K. Takahashi, S. Aratani, Y. Yamauchi	Journal of Materials Science Letters, Vol. 11, 1992
Fracture and Failure in Glass	M. Brungs	Materials Forum, (1955)
Taking a closer look at glass strength data	I. Calderone, W. Melbourne	
Investigation of ways to strengthen glass tubes	M. Skakunov, B. Bakulkin, E. Ezerskii	
The 'analysis of pieces' method of analysing the causes of the spontaneous breakage of toughened glass insulators	H. Hansheng, M. Dingfu, C. Guorong	Glass Tech., Vol 32, No. 5, 1991
Cascading fracture in a laminated tempered safety glass panel	T. Sakai, M. Ramulu, A. Ghosh, R. Bradt	International Journal of Fracture, Vol. 48, 1991
Testing and Failure of Windows in Adverse Environments		
Dynamic Response of Window Glass Plates under Explosion Overpressure	D. Makovicka, P. Lexa	Research Institute of Occupational Safety
Application of the response probability density function technique to predicting the probability of sonic-boom glass breakage	R. Hershey, T. Higgins, E. Magrab	J. Acoust. Soc. Am., Vol. 55, 1974.
Analysis of Glass Breakage in window Accidents	C. Drury, K. Brodsky, G. Dargush	
On-Site Investigation of Spandrel Glass Microenvironments	R. Behr	Building and Env., v.30 1995
Architectural Glazings: Design Standards and Failure Models	A. Fischer-Cripps, R. Collins	Building and Env., V30, 1995
Failure of cladding, glazing and structural elements: High-rise buildings	J. Minor	CWOWE IV-Nov. 19-20, 1984
Fire-Induced Thermal Fields in Window Glass II- Experiments	A. Joshi, P. Pagni	Fire Safety Journal, 22, 1994

Testing and Failure of Windows in Adverse Environments <i>(continued)</i>		
Dynamic Racking Tests of curtain wall glass elements w/ in-plane and out-of-plane motions	R. Behr, A. Belarbi, J. Culp	Earthquake engineering and Structural dynamics, Vol. 24, 1995
Reliability analysis of window glass failure pressure data	R. Behr, M. Karson, J. Minor	Structural Safety, 11, 1994
Wind Speed-Damage in Correlation in Hurricane Frederic	K. Mehta, M ASCE, J.Minor, F. ASCE, T. Reinhold	
The Fracture of Glass by Impact	A.Woodward, J. Field	
Window Glass in windstorms	J. Minor, M. ASCE, W. Beason	Journal of the Structural Division, 1976.
Safety of glass panels against wind loads	C.V.S. Kameswara Rao	Short Communication
Climatological Assessment of Airblast Propagation from Explosion Tests at White Sands Missile Range	J. Reed	Sandia Report, 1986
Strength of window glass plates subjected to rapid loading	H. Pal	Texas Civil Engineer, 1988
The response of buildings to accidental explosions	R. Mainstone	
Breakage of Glass Window by Explosions	D. Pritchard	Journal of Occupational Accidents
The Response of Glass Window to Explosion Pressures	R.J. Harris, M.Marshall, D. Moppett	I. Chem. E. Symposium series, no. 49
Effects of Pressure Waves	no author listed	
Thermal Tempering		
Fundamentals of Tempered Glass	R. McMaster	Ceram. Eng. Sci. Proc. Vol. 10, 1989
Deferred processes in the Fragmentation of tempered glass	P. Acloque, M. Morain	Verres et Refr. Vol. 20, 1966
Strength Degradation of Thermally Tempered Glass Plates	D. B. Marshall., B. R. Lawn	J. Am. Ceram. Soc. Vol. 61. No.1-2, pp. 21-27 (1978).
Strengthening of Glass	F. Ernsberger	The Glass Industry, Sept. 1966.
What is Tempered Glass?	R. Gardon	Glass Science and Technology, Vol. 5, pp. 146-157.
Fracture of Tempered Glass	J. Barsom	J. Am. Ceram. Soc., Vol. 51, pp. 75-8, 1968.
Crack Propagation in Tempered Glass	S, Aratani, K. Oginoh, M. Takatsu	J. Soc. Materials Science, Japan
Effect of Tin Oxide Coating on the strength of Tempered Glass	J. Chang, J. Zhou	

Producing High Strength Glass by Liquid Quenching in an Ultrasonic Field	A. Boguslavskii, O. Khalizeva	
Economical Cooling Modes in Air-Jet Thin Glass Quenching	A Shutov, V. Popapov., V. Agibalov	
A Nomogram for Glass Cooling	A. Shutov, E. Sakulina	
The Strength of Thin, Thermally Polished, Toughened Glass	A Shutov, A Maistrenko, I. Kazadova	
Fracture Strength of Tempered Glass	J. Chang, J. Chou	Journal of Non-Crystalline Solids, Vol. 52, 1982
Tempering Glass With Modulated Cooling Schedules	R. Gardon	J. Am. Ceram. Soc. Vol 71, 1988

An upcoming publication related to this Laboratory Research and Development project is E. K. Beauchamp's "Fracture Behavior of Double-Ion-Exchanged Glass," to be published in the Proc. of the Fractography of Glasses and Ceramics Conf. IV, Alfred, NY, July 9-12, 2000.

Appendix

ESP (Engineered Stress Profile) Glass – Unique Opportunities for Performance and Reliability

by

S. Jill Glass, Ed K. Beauchamp, Clay Newton, and Ron Stone

ESP (Engineered Stress Profile) Glass - Unique Opportunities for Performance and Reliability

Motivation—There are many aspects of glass that we take for granted such as its transparency, its formability, and the abundance and cheapness of the raw materials. One property not taken for granted is its low strength and reliability. Glass is the classic brittle material with extreme sensitivity to the presence of surface flaws and catastrophic failure. Once the stress exceeds that required to activate the most severe flaw, which is not easily detectable, failure occurs instantaneously without warning. The wide flaw size distribution in glass leads to a wide fracture strength distribution. Flaws are either intrinsic to the processing of the glass or are surface damage introduced after processing. As a result glass is rarely considered for structural applications and large safety factors are built into any design where strength and reliability are critical. The introduction of residual surface stresses is commonly used to increase the strength and modify the fragmentation behavior of safety glass. The small cube-like fragments of pre-stressed glass are far less lethal than the large dagger-like shards that are typical of the fracture of annealed glass. Unfortunately the surface modification of pre-stressed glass does not increase reliability; it often increases the strength scatter even further.

Accomplishment--A new approach for strengthening and dramatically increasing glass reliability has been developed and implemented for both specialty compositions and for regular soda lime silicate (SLS) glass. Regular ion-exchanged glass and thermally tempered glass have the compressive stress maximum right at the surface. The new process uses a two-step ion exchange. During the 2nd step some of the large ions introduced in the 1st exchange step are removed, partially relieving the surface stress and producing a compressive stress maximum below the surface. At significant levels of the applied stress (relative to the fracture strength) a single surface crack starts to grow into the glass. The crack encounters increasing resistance to

propagation as it penetrates into the increasing compressive stress field. Finally the magnitude of the compressive stress arrests the crack and it turns away from its initial trajectory. As the applied stress increases further another surface crack begins to propagate and is then arrested in the same manner. Fig. 1 shows ESP glass that contains an array of arrested cracks. This process is repeated until a critical value of the applied stress is reached. The failure strength is not dependent on the size of the worst flaw, but on the details of the stress profile. Thus the strength distribution is not dependent on the flaw size distribution and is very narrow compared to that of regular glasses and ceramics. A typical glass has a low Weibull modulus, e.g., $m=5-10$. ESP glass has values as high as 60. The two-step ion exchange process provides broad flexibility in terms of engineering the stress profile to optimize, strength, reliability, and fragmentation behavior for different glass compositions. We will continue to improve our ability to engineer stress profiles and glass behavior to satisfy new application requirements.

Significance—For the first time we have a glass that is both strong and dependable, cracks non-catastrophically, and fractures into small fragments. A designer's confidence in the glass's ability to survive or fail at a given stress is increased significantly as shown in Fig. 2. In an application where the glass must sustain 80% of the average failure stress, ESP glass with $m=60$ has an only one two in one million chance of failing. In contrast regular annealed glass has a 30% failure probability. ESP glass also shows remarkable resistance to contact damage, the primary factor in strength degradation for glazing applications where wind-borne debris causes damage. Engineered stress profiles can be produced with processes that allow great flexibility with respect to glass composition and performance optimization, providing unique opportunities for new glass applications.

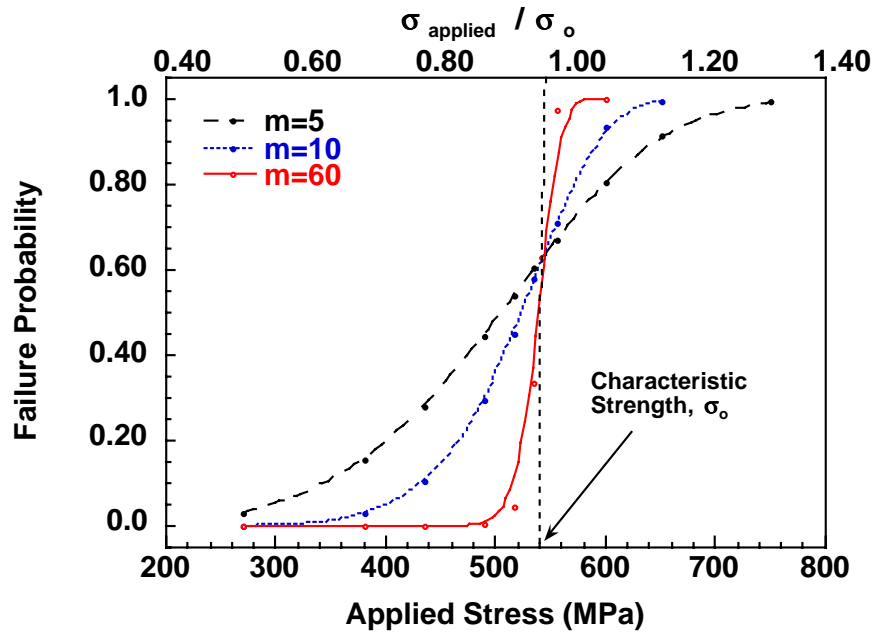


Fig. 1. Failure probability vs. applied stress for various Weibull moduli, m . ESP glass, with $m=60$, has a dramatic increase in failure probability only at the average failure stress, in contrast to regular glass ($m=5-10$), which has a high failure probability at stresses below the failure stress.

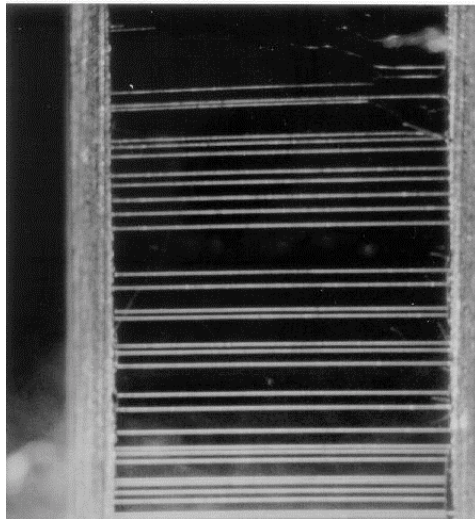


Fig. 2. Soda lime silicate glass with non-catastrophic cracks formed prior to failure.

Sponsors for related work include: Halliburton Energy Services, Advanced Concepts and Applications, Weaklink Feasibility Study Group, and the USAF Force Protection Battlelab.

Contact: S. Jill Glass, Ceramic Materials Dept. 1843
 Phone: (505) 845-8050,
 Fax: (505) 844-4816
 E-mail: sjglass@sandia.gov

Distribution

1	MS 0188	Donna Chavez, 1030
1	MS 0769	Dennis S. Miyoshi, 5800
25	MS 0782	Rudolph V. Matalucci, 5861
1	MS 0782	Sharon O'Connor
1	MS 0782	Gordon J. Smith
1	MS 0889	Clay Newton, 1843
1	MS 0889	Edwin K. Beauchamp, 1843
25	MS 0889	S. Jill Glass, 1843
1	MS 0889	Willard Hunter, 1314
1	MS 0959	Ron Stone, 14192
1	MS 1411	Duane Dimos, 1843
1	MS 9014	Al Baker, 2267
1	MS 9056	Bob Gallagher, 9056
1	MS 9018	Central Technical Files, 8945-1
2	MS 0899	Technical Library, 9616
1	MS 0612	Review & Approval Desk, 9612, For DOE/OSTI